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THE UNIVERSITY OF ALBERTA

THE DEBYE TEMPERATURE AND HARDNESS OF COPPER-NICKEL ALLOYS

A Thesis

Submitted to the Faculty of Graduate Studies
In Partial Fulfilment of the Requirements
for the Degree of Master of Science

DEPARTMENT OF MINING AND METALLURGY

by

DONALD HARRY TIMBRES

EDMONTON, ALBERTA

APRIL, 1964

UNIVERSITY OF ALBERTA

FACULTY OF GRADUATE STUDIES

The undersigned certify that they have read and recommend to the Faculty of Graduate Studies for acceptance, a thesis titled

THE DEBYE TEMPERATURE AND HARDNESS OF
COPPER-NICKEL ALLOYS

submitted by DONALD HARRY TIMBRES

in partial fulfilment of the requirements of the degree of Master of Science.

ABSTRACT

The Debye temperature of copper-nickel alloys obtained by x-ray intensity measurements of the 800 reflection is described. The 'cube' texture (100) [001] produced in the copper-nickel alloys facilitated the separation of the high order reflection from the background intensity.

Values of micro-hardness (DPH) have been found for the copper-nickel alloys and do not show a marked dependence on the applied load. Meyer exponents calculated for the copper-nickel system varied but no general trend was observed.

A correlation between the Debye temperature and hardness values was sought but no finite relationship could be found.

ACKNOWLEDGEMENTS

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INTRODUCTION

The frequency spectrum of the coupled vibrations of atoms in a crystal lattice has been the center of considerable interest for many years. The first and most simple theory to explain the spectrum was due to Einstein (Kittel 1956, for summary) who assumed all the atoms to vibrate with the same frequency, so that the vibrational spectrum was a single line. The next development of the theory was due to Debye who considered the problem from the quite different point of view, of the vibrations to be expected in a monatomic solid considered as an elastic continuum. Although a number of calculations, with varying degrees of approximation, have been made since Einstein and Debye considered the problem, the most widely used approximate frequency spectrum is still the parabolic distribution introduced by Debye. This frequency spectrum is usually described in terms of the characteristic, or Debye temperature, Θ, which is related to the maximum vibration frequency of the lattice v_m by $\Theta = hv_m/k$ (h Planck's constant, k Boltzmann's constant).

The thermal vibrations of the atoms are of considerable importance in the scattering of x-rays, for any departure from strict regularity in the arrangement of the scattering particles will tend to weaken the interference maxima, and to increase the radiation scattered in other directions. The effect this thermal vibration has in reducing the intensity maxima was first studied by Debye who introduced a temperature factor to account for the decrease in the interference maxima with temperature.

[illegible]

[illegible]

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The temperature factor is related to the absolute temperature and the Debye temperature of the crystal.

The thermal energy results from the atomic vibrations, which are controlled by the forces holding the atoms together. These same forces determine the elastic properties, and consequently these are related to the Debye temperature. The metal's resistance to permanent deformation (hardness) is also controlled by the forces holding the atoms together; so one might expect a connection between hardness and Debye temperature through the elastic parameter.

The object of the work to be described here is two-fold: first to determine the Debye temperature in various copper-nickel alloys by measuring the change in the intensity maxima at two known temperatures; second, to obtain representative hardness values of the alloys so that a relationship can be sought between Debye temperature and hardness.

THEORY

(a) The Determination of Debye Temperatures by X-ray Measurements

The reflection of x-rays as formulated by Bragg assumes the lattice points to be stationary and possess a regular pattern throughout the crystal. This assumption is not valid physically, as the atoms vibrate continuously, even at absolute zero. The thermal agitation of the atoms in the crystal lattice causes small and irregular displacements of the atoms from the lattice planes. The contribution of these vibrating atoms to the reflection maxima will therefore cause the intensities to be less than they would have been had all the atoms been at rest. It is evident that the higher the temperature the smaller will be the intensity of a given maxima, because the vibrations of the atoms cause a decrease in the phase relationships of the reflected x-rays.

Much of the subject matter of the following paragraphs is discussed in great detail by James(1948, Chapter 5) where derivations of the equations used will be found.

When Debye originally considered the vibrational spectrum, the atoms were supposed to oscillate about fixed positions of rest, to which they were bound by a quasi-elastic force, and the Maxwell-Boltzmann distribution law was used to obtain the probability of a given configuration of all the atoms of the lattice. The intensity of the spectrum of a given order for a known configuration can be calculated. If this calculated intensity is now multiplied by the probability of the configuration, and the resulting

product summed over all possible configurations, the average intensity of the spectrum, which is what is observed, is obtained.

However, the atoms are not bound to fixed positions of equilibrium, but to one another, and Debye amended his calculations, basing his work on the ideas of Born and Karman, in which the heat-motions are considered as a series of elastic waves in the crystal. He found that the integrated intensities of the interference maxima should be multiplied by a factor exp(-M), where

$$M = \frac{6h^2}{mk\Theta}\left(\frac{Q(x)}{x} + \frac{1}{4}\right)\frac{\sin^2\phi}{\lambda^2}$$

m = atomic weight of an atom

h = Planck's constant

k = Boltzmann's constant

Θ = Debye temperature of the crystal

$x = \frac{\Theta}{T}$

T = absolute temperature

$Q(x)$ = Debye function

$$= \frac{1}{x}\int_0^x \frac{u\,du}{\exp(u) - 1}$$

ϕ = Bragg angle

λ = wave-length of the radiation

The fraction $\frac{1}{4}$ added to $Q(x)/x$ makes allowance for the existence of zero-point energy, but its presence or absence does not matter for the purpose to which we apply this formula.

Later work by Waller (1923) indicates that for a simple lattice the factor should be $\exp(-2M)$ instead of $\exp(-M)$. Waller explained that the necessity for the extra factor of 2 was due to the counting of the normal modes of the vibrating lattice. The factor $\exp(-2M)$ is known as the temperature effect, or Debye-Waller temperature factor.

By measuring the integrated intensity of a Bragg reflection at two known temperatures the value of the Debye temperature, Θ, may be obtained. If I(1) and I(2) are the integrated intensities of a given reflection at temperatures T(1) and T(2), then

$$\frac{I(1)}{I(2)} = \frac{\exp(-2M(1))}{\exp(-2M(2))} \tag{3}$$

All other factors which enter the determination of the integrated intensity are multiplicative and cancel.

Using equations 1 and 3 it follows that

$$\ln\frac{I(T1)}{I(T2)} = \frac{12h^2}{mk\Theta}\left(\frac{Q(x2)}{x(2)} - \frac{Q(x1)}{x(1)}\right)\frac{\sin^2\phi}{\lambda^2} \tag{4}$$

For an alloy the mean atomic weight is used for m.

Debye in his theory neglects the variation in Bragg angle due to the change in the lattice spacing with temperature, but in this work we have considered this change. Θ also varies slightly with temperature, and

the correct use of this formula would require the knowledge of the Debye temperature at one of the temperatures.

From equation 3, it can be seen that accurate measurements of the integrated intensities are necessary. Single crystals would be the obvious answer to fulfil this requirement, as they provide the strongest Bragg scattering. However, as single crystals are very difficult to grow, let alone orient, a simpler technique may be used, in which simulation of single crystals can very easily be obtained in certain face-centered cubic metals. Peak to background ratios of the order of 30 to 1 (800 reflection) have been obtained using this technique, which has considerably improved the precision of separating the Bragg reflection from the background.

In this work only the 800 reflection is measured because the ratio $\ln \frac{I(T1)}{I(T2)}$ is larger for higher order reflections and the level of background is more uniform at the higher scattering angles.

The method for determining the integrated intensities is described later.

(b) Micro-hardness

Hardness is a property of which we are most conscious, yet a precise definition depends entirely on the method of measurement. Probably the best general definition is one given by Ashby (1951), "hardness is a measure of the resistance to permanent deformation or damage".

The methods most widely used in determining the hardness of metals are static indentation methods. These involve the formation of a permanent

indentation in the surface of the metal to be examined, the hardness being determined by the load and the size of the indentation formed.

There is a wide range of hardness tests and a wide range of testing conditions, the main variants being the nature of the indenter and the load applied. Because of the variety of materials to be tested, it is necessary to make the indenter from a very hard substance to prevent its deformation by the test piece; and for this reason either a hardened steel sphere or a diamond pyramid or cone is employed.

In the work described in this thesis, hardness measurements were required on individual grains; and the apparatus chosen was a Reichert Micro-hardness Tester. The instrument, although very delicate, has a high degree of accuracy, both in the application of the load and the measurement of the indentation produced. The hardness determined by this instrument is measured in kilograms per square millimeter, and involves three factors: the load, the size of the impression and the geometry of the indenter. The Reichert Micro-hardness Tester employs a diamond indenter having the form of a square-base pyramid with an apex angle (α) of 136 degrees.

It is imperative at this point to make the distinction between micro-hardness and other forms of hardness. Micro-hardness is reserved for indentations(with square-base pyramid) less than about 50 microns in diameter, which corresponds to loads of 1-100 grams. This region differs from tests carried out with medium loads(200-300 grams), and macro-

hardness testing with loads over 3000 grams. Indentations made with hardened steel balls or diamond cones fall into the region of macro-testing and will not be considered here.

The indentation hardness number in the Reichert test is the value of the force acting on the indenter, expressed as the weight (P) in kilograms, which produces in the sample a permanent indentation with a superficial area (M) of one square millimeter. The hardness, known as diamond-pyramid hardness (DPH), has units of force per unit area. The DPH may be determined from the following equation

$$\mathrm{DPH} = \frac{P}{M} \qquad \mathrm{kg/mm^2} \tag{5}$$

The value of the force used is known directly as a weight; the value of the superficial area of the resulting indentation can only be calculated on the basis of measurements. Since it is assumed that the diamond indenter is not deformed by the penetration, the superficial area of the pyramid shaped indentation can be calculated if the diagonal (d) of the square base is measured.

The superficial area (M) of a square pyramid with known apex angle (α) and a known diagonal (d) of the base is given by

$$M = \frac{d^2}{2 \sin \frac{\alpha}{2}} \tag{6}$$

In the Reichert Micro-hardness Tester $\frac{\alpha}{2} = 68$ degrees. The value of the superficial area of the indentation is then given by

$$M = \frac{d^2}{2\ \sin 68^\circ} = \frac{d^2}{2(0.92720)} = \frac{d^2}{1.8544} \tag{7}$$

Then DPH $= \frac{P}{M}$, becomes $1.8544\ \frac{P}{d^2}$ kg/mm^2.

If P is in grams, and d is in microns, then

$$\text{DPH} = 1854.4\ \frac{P}{d^2}\ \text{kg/mm}^2 \tag{8}$$

(c) Recrystallized Texture in Copper-Nickel Alloys

The phase diagram of the copper-nickel system shows a single-phase solid solution over the entire range from pure copper to pure nickel. The crystal structure of this spectrum of solid solutions is face-centered cubic.

In certain face-centered cubic metals and alloys, large crystals may be obtained, under certain conditions, by deforming a fine-grained polycrystalline specimen and annealing at a high temperature. The recrystallized texture which forms on annealing has a high degree of preferred orientation and is known as the 'cube texture' (100) $[001]$. The 'cube texture' is described as one in which a plane of the form $\{100\}$ is parallel to the rolling plane, and a direction of the form $\langle 001 \rangle$ is parallel to the rolling direction.

Baldwin (1942) showed that the texture occurred in copper after heavy deformation, by cold rolling, and subsequent annealing at a high temperature (1000°C). His graphs show a relationship between the percentage of cubically aligned grains and percentage reduction of the material.

The greater the reduction of the polycrystalline material the greater the preferred orientation possible with increasing annealing temperatures.

The preferred orientation obtained in this work on copper and the copper-nickel alloys largely follows Baldwin's technique.

The derivation of the theory for the cube texture will relate to copper, but the same orientations exist for other metals and alloys of which nickel is one (because Bragg reflections could only be obtained from planes of the type $\{100\}$ in the copper-nickel alloys, the theory obviously holds for these alloys).

The structural changes that take place in many face-centered cubic metals and alloys when they are very heavily cold rolled and annealed have been throughly studied (Barrett 1952 for summary). A highly deformed texture must be obtained before recrystallization will give the cube texture and normally, the metal or alloy must be fine-grained and homogeneous before cold working. During the cold rolling operation, deformation occurs first by slip, but later, as the reduction increases, the plastically deformed grains begin to align themselves in particular directions. It is during this heavy cold reduction that the grains obtain a strong preferred orientation. The reduction in thickness must be greater than 95 percent before total alignment occurs on subsequent annealing. Annealing this deformed material at low temperatures (300°C-400°C) causes the material to recrystallize in the 'cube texture'. Additional heating to within a hundred degrees of the melting point results in an increase in the grain

size. The growth of the grains is brought about by movement of the boundary layers between two non-parallel regions. This is acheived when one grain which has a size larger than its surrounding neighbours grows at their expense.

Such large grains have been readily obtained in the copper and copper-nickel alloys studied in this work.

APPARATUS

(a) X-ray Diffraction System

The apparatus used in obtaining the integrated intensities (Figure 1) was designed and built by Goldak (1964), who describes the entire system in detail. While much of the theory behind the electronics of this system is not familar to me, the mechanics of its operation are understood. Therefore, only a brief discussion of the main components of the unit is presented below.

Intensity measurements were made on a Rigaku-Denki, model D3-F generator—SG-11 Rigaku-Denki horizontal circle diffractometer combination, using Zr-filtered MoK radiation. The x-ray tube voltage and current are stablized to 0.01 percent.

A Norelco scintillation counter model 52245, with a thallium-activated sodium iodide crystal, which is electrically connected to a scaler, records the number of pulses from the counter. The counter is positioned at a fixed value of two theta for a set time to make an accurate count of the reflected photons, it may then be moved to new angular position and the operation repeated. The movement is entirely automatic and only requires an initial setting at the required angle for commencing scanning.

Movement of the counter is by a stepping motor where one 'step' corresponds to 0.01 degrees two theta. The design is such that scanning may be preformed either continuously or one step at a time, in either the forward or reverse direction.

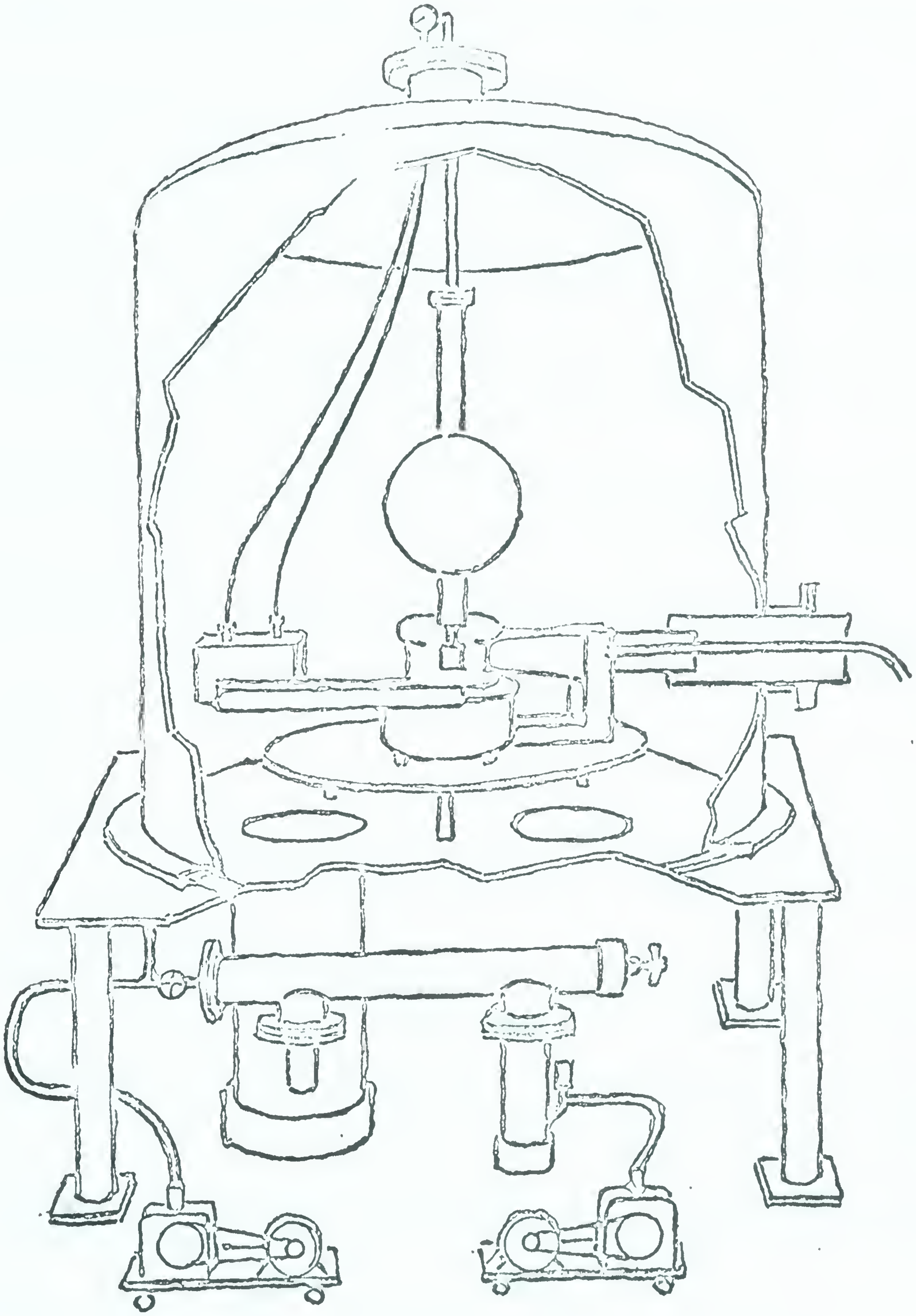

Figure 1. Cutaway View of System (Goldak 1964)

This method of obtaining a diffraction pattern is very slow but yields more precise measurements of intensity than a continuous 'scan' over the same range of two theta.

Pulses from the scintillation counter, before going to the scaler, are passed through a pulse height analyzer, whose function is to pass pulses within a given amplitude range and to reject pulses of greater or lesser amplitudes. The pulse height analyzer removes low energy noise pulses and low energy pulses produced by wavelengths longer than the desired wavelength. It also removes pulses of greater amplitude produced by wavelengths shorter than the desired wavelength, which may be higher order wavelengths reflected at the same angular position as the desired wavelength.

The lower limit of the pulse height analyzer in this work was set at 12 volts with a 'window voltage' of 10 volts. This accepts approximately 90 percent of the MoK radiation.

The pulses received from the pulse height analyzer are then fed into a Beckman 7061 counter (the scaler), which can be set to admit pulses from the scintillation counter for a time interval from 1 millisecond to 10 seconds. In this work the Beckman was set to receive pulses for 10 seconds. The accuracy of the time interval is stated to be 1 millisecond. The noise level, the pulses obtained when the x-ray generator is shut off, amounted to 1 count in 10 seconds.

From the process of scanning a given reflection, a large amount

of data is obtained—one reading for every 0.01 degrees two theta. To record this large volume of results, the Beckman counter was read out on an IBM 26 card punch, which recorded the intensity and angle at which this intensity was obtained, on IBM cards. Each card has five intensity and angle measurements recorded on it. These cards are then readily accepted by an IBM 1620 computer for analysis. The starting two theta angle must be known before scanning is commenced as the angle that is recorded on the IBM cards, i.e. the number of 'steps' taken by the scintillation counter, shows only successive numbers beginning from zero. The keys of the IBM 26 card punch are activated by solenoids mounted in a frame over the keyboard, the pulses being obtained from the Beckman counter.

The entire diffractometer (Figure 1) is enclosed in a steel bell jar of diameter 42 inches and height 58 inches. The bell jar is placed on a 1 inch thick steel table top, the vacuum seal being provided by two neoprene rings of dimensions 0.375 inches wide by 0.375 inches thick. The system, which utilizes a 10 inch oil diffusion pump backed by a 4 inch oil pump, is capable of a vacuum of 10^{-6} mm. Hg. Initially the system is 'roughed' out with two mechanical pumps. Service entry into the chamber is through a 14 inch porthole in the table.

Because of the deflection of the steel table top when the chamber is evacuated the diffractometer is mounted on a second steel table supported by three leveling legs (Figure 1). Therefore any movement of the steel

table moves the entire diffractometer and does not alter the optics of the system.

A cryostat (Figure 1) mounted directly on the diffractometer by three pillars serves a two-fold purpose; it acts as a holder to which the specimens can be clamped, and makes low temperature (liquid nitrogen) intensity measurements of the specimen possible. The inside of the cryostat is open to the atmosphere through a flexible copper tube and it is through this copper tube that the liquid nitrogen is added. The cryostat holds approximately two liters of liquid nitrogen which is sufficient for 24 hours of continuous running when the vacuum is 10^{-6} mm. Hg. A copper block is attached to the cryostat by a glass-to-metal seal, which insures that the specimen is at the temperature of liquid nitrogen. The cryostat has been positioned on the diffractometer so that flat specimens clamped to the copper block have their surfaces tangential to the focusing circle and at equal distances from the x-ray source and the receiving slit. A 1 degree slit system is used in all measurements.

The temperature is measured with a chromel-alumel thermocouple, and a 4725 Rubicon Potentiometer which may be read to 1 microvolt. An ice junction is used as the reference point.

(b) The Reichert Micro-hardness Tester

This apparatus was designed for use on the Reichert Universal Camera-microscope type MeF. A very full description has been given in a pamphlet issued by the Reichert Company called 'MICRO-HARDNESS,

Its Theory and Practice with the Reichert Micro-hardness Tester'. A brief description of some of the principal components of this instrument, and its calibration is given below. The instrument is shown in Figure 2.

The working part consists of two torsion bars (9a and 9b) arranged one above the other on a carrier (8). Each bar carries a fork (10a and 10b) on which the pressure member (12) is fitted between two leaf springs (11a and 11b). Fixed to the pressure member is a diamond indenter (14) in the shape of a square pyramid and a objective lens (13) used to view the specimen surface. The pressure member, the two forks and two torsion bars together form a torsion balance for determining the load exerted on the indenter. The mechanics of the pressure member is such that either the diamond or objective lens can be put into use by a lever connecting the two. A measuring eyepiece complements the objective, and in its field of view can be seen two wires which are movable towards one another by means of micrometer screw, the amount of the movement being shown on a drum divided into 100 units. Each wire contains a right angle, and the two wires form the four sides of a square (Figure 3). For each complete revolution of the drum a horizontally moving coarse scale travels in the upper part of the field of view of the measuring eyepiece, just above the wire square. In addition to their use for measurement, the wires fulfil two other functions: when fully closed, G and C coincide at the point at which the diamond penetrates the specimen; if suitably open, one of the intersections, B or D, acts as a reference point on the weight scale,

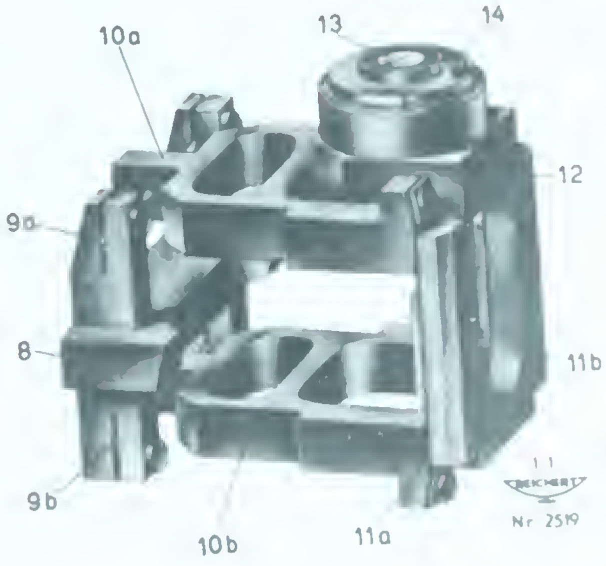

Figure 2. Interior View of Upper Portion of Reichert Tester

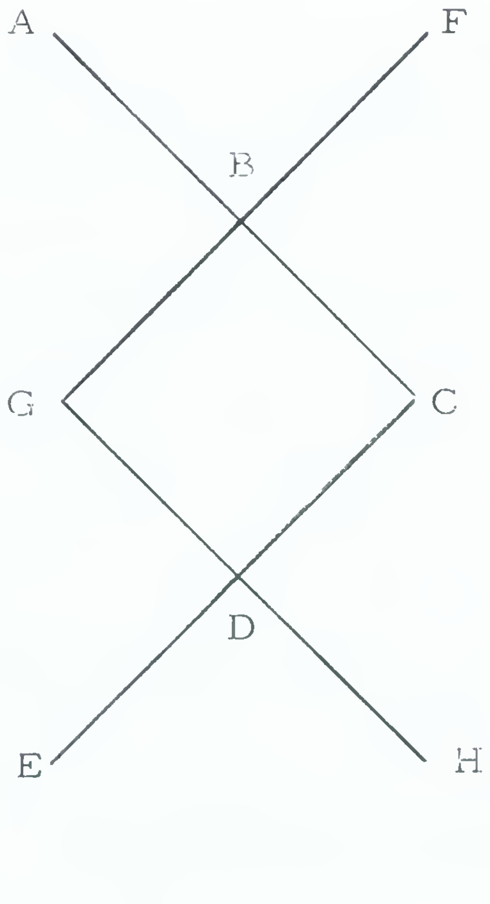

Figure 3. The Two Rectangular Wires for Measuring Impressions

which will be explained below.

The calibration of the divided drum is obtained by focusing on an objective micrometer in which the distances between successive markings are known. The distance in the objective micrometer, which corresponds to one division on the divided drum, was found to be 0.161 micron.

When the diamond is put into play the force with which the diamond presses upwards against the specimen is equal to the force of equal value with which the specimen presses the diamond downwards. This downward directed force acts in just the same way as if a weight of given size were to act from above on the hardness tester. It is precisely this principle that is used to calibrate the load with which the diamond presses against the specimen.

As was stated above, when the objective lens is in play the distance between corners of the indentation can be measured, i.e. the distance between the corners of the right-angled wires; but when the diamond is moved into position another scale is observed, which shows the load applied to the diamond. It is this scale, known as the weight scale, that is calibrated by applying known weights and noting the deflection of the scale. By placing the intersecting point B on the zero division of the weight scale and adding known weights a calibration graph can be obtained as is shown in Figure 4. The fact that a calibration must be made is due to the displacement of the weight scale not being linearly proportional to the weight employed. The relationship can be expressed in the form

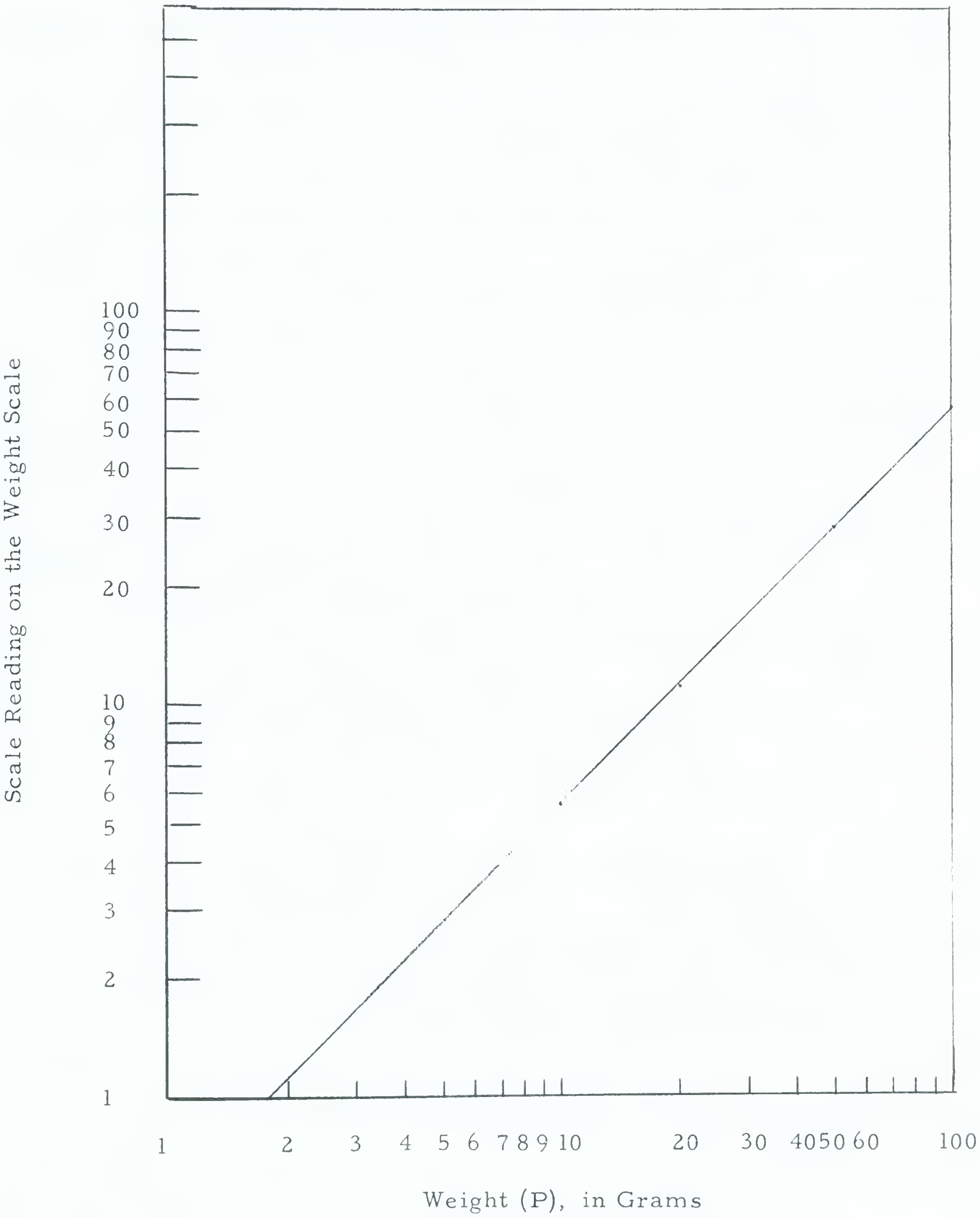

Figure 4. Calibration Curve for Weight Scale

[illegible]

[illegible]

of a curve, but when shown on logarithmic paper this plots as a straight line. Therefore the known force with which the indenter penetrates the material may be read off this graph.

When the weights are removed, the weight scale returns to its zero position.

Before any indentations are made, the weight scale is always checked to see whether any deviations have occurred due to dust, dirt or friction from the moving parts. The length scale does not need to be checked, however, as the work is always performed with the same measuring eyepiece.

EXPERIMENTAL PROCEDURE

(a) Sample Preparation

All samples were induction melted in impervious recrystallized alumina crucibles in a positive argon atmosphere. Before an alloy was melted the system was evacuated to a pressure of 10^{-5} mm. Hg. initially, then purged twice with argon. Spectrographically pure copper and nickel from Johnson, Matthey and Company was used in the preparation of the alloys. Analyses are given in Appendix 1.

Each molten alloy was allowed to mix under the influence of the induction currents for five minutes and cooled in the crucible. To insure further homogenity each sample was cold rolled to approximately 50 percent of the original thickness, then annealed in an argon atmosphere for 12 hours at 1000°C. Metallographic examination showed no coring or composition variation.

From each of these samples, two portions were cut, one for analysis and the other for further reduction. The analysis for each alloy is shown in Appendix 1. Samples 1 by 1/4 by 1/4 inches were then cold rolled another 96-98 percent. The softer samples (copper-rich) showed greater reduction (98 percent) than the nickel-rich samples. With these particular pure metals and alloys 98 percent reduction was the maximum reduction possible—a limitation of the rolls.

The rolled samples were then annealed in a quartz tube at a controlled temperature of 1000°C for 8 hours in a flowing atmosphere of argon. The

dimensions of the samples for annealing were 1.5 by 0.75 inches, the thickness varying from 0.004 to 0.006 inches. Only one specimen was annealed at a time, with each sample supported within the furnace tube on a molybdenum sheet.

After removal from the furnace each sample was treated with a solution containing 50 percent nitric acid and 50 percent acetic acid by volume to make the grains visible.

(b) Mounting Samples for X-ray Measurements

In order for x-ray intensity measurements to be obtained, each sample was mounted on an aluminum 'backing' block to give the sample rigidity and to insure that the irradiated surface was flat. The aluminum 'backing' blocks were cut from 0.25 inch flat aluminum plate, and polished to insure a flat surface. The specimen was mechanically clamped to the block and to the cryostat (already shown). This method of mounting the specimens for intensity measurements was found to be far superior to a method tried earlier where the specimens were glued to the surface of the aluminum blocks and then clamped to the cryostat. The glueing method required a number of backing blocks to be prepared while the former required only one, and gave the added assurance that all measurements were taken under similar conditions.

(c) Preparation of Samples for the Hardness Measurements

From each of the bulk samples prepared, a portion was also removed

for micro-hardness measurements. This portion, which has been reduced 50 percent and annealed at 1000°C in an argon atmosphere, provides a sample which is homogeneous for hardness measurements. This fact was born out by the consistency of the results and the low standard deviation obtained.

Each of the specimens was mounted in 1.25 inch bakelite molds and polished on four adhesive-backed silicon carbide abrasive papers of increasing fineness (grits 240, 320, 400, and 600). This procedure was adopted in order to minimize the depth of the work hardened layer in the specimen. At no time during the polishing procedure did the specimens contact a coarse abrasive belt.

After removing from the 600 grit paper, the specimen was placed on a low speed rotating lap polisher with diamond abrasive, lubricated with a special lapping oil to insure uniform dispersion. This was the only time during the cycle that the specimen was placed on the lap polisher.

The specimens were then placed on a Fisher vibratory polisher with a Buehler AB Kitten-Ear Broadcloth and a slurry of Linde B (0.05 micron alumina) abrasive and distilled water. The polishing bowl in which specimens are placed has a rotary pulsating motion and a vertical motion. On account of these motions, samples move around the bowl in a counter-clockwise direction. Since frictional forces on the inner and outer radii of the samples are not in balance, the sample also rotates about its own vertical axis while moving around the bowl, thus assuring non-directional polishing.

However, in order for any polishing action to be obtained, the specimen is weighted with a 350 gram weight, otherwise its inertia would prevent any slipping between the specimen and the cloth. Although the Fisher vibratory polisher is capable of polishing 20 specimens at one time, only one sample was dealt with at a time, because of the varying hardness of the specimens.

The setting of the rheostat control to control polishing speed is critical, as too low a setting causes directional polishing while a high setting bounces the specimens and little polishing results.

The composition of the slurry is also critical in that too dry a slurry causes scratches, while too wet a slurry causes little polishing. The required constitution was determined by the 'pond' which flows with the sample as it rotates around the periphery of the polishing bowl, and usually involved a mixture of five ounces of alumina and 100 ounces of distilled water.

Each specimen required approximately 10 to 15 minutes in the bowl to remove scratches remaining from the former polish. The time varied with the hardness of the material.

The samples were then etched first with a ferric chloride solution (5 grams $FeCl_3$, 50 ml HCl, and 100 ml distilled water), followed by a nitric acid etch (equal volume solution of nitric and acetic acid). The double etch revealed grain contrast and more effectively removed disturbed metal.

The mounted samples were then replaced on the vibratory polisher and allowed to polish for an additional 10 minutes. This time was found sufficient to remove the effects of the etched surface. The sample was then re-etched with the two etches and placed on the cloth for a third polish. In total the specimen was polished and etched four times to remove or minimize any traces of the work hardened surface.

The reason for polishing and etching four times arose from trials, which showed that micro-hardness measurements taken after each successive polish-etch revealed an increase in the average diameter of the indentation. However, after the fourth polish-etch, no increase in the average diameter of the indentation from that of the third polish-etch was observed. This increase in average diameter was measured from 50 indentations recorded after each polish-etch procedure.

(d) Intensity Measurements

Measuring the values of the integrated intensities requires the separation of the Bragg reflections from the 'background'. As the ratio of peak to background intensity increases, the error caused in separating the Bragg reflection from the background intensity decreases, because it is easier to measure a large effect than a small one. Because of the preferred recrystallization texture obtained in the copper and copper-nickel alloys,this separation is possible with only a small error even for high order reflections. The reflection chosen for study in the copper and copper-nickel alloys is 800 in which peak to background ratios of 30

to 1 are obtained. All values of the integrated intensities in this work pertain to the 800 reflection.

For each alloy, the 800 reflection is scanned five times at room temperature, five times at liquid nitrogen temperature, and twice again at room temperature. Scanning the peak again at room temperature is used as a check, to see if the conditions present in the initial room temperature runs still prevail.

For all intensity measurements a molybdenum x-ray tube is operated at 40 kv and 15 ma. This setting remains unaltered for each alloy during the 12 scans. A one degree slit system and a Zr filter are used for all intensity measurements. Because the scanning is entirely automatic, all that is required to scan a peak is to set the scintillation counter at an angular distance to one side of the Bragg reflection and to stop it after it has completely traversed the reflection and some background. The distances used in this work are approximately 5 degrees, which gives an 11 degree scan in total. In using this range for scanning a peak, a representative picture of the background is obtained.

When making intensity measurements the system is allowed to attain equilibrium before scanning begins. The temperature is recorded before and after every scan, and small fluctuations in the temperature are averaged. In all runs the vacuum is 10^{-6} mm. Hg. or better.

The chromel-alumel thermocouple used to record temperature was checked against a calibrated chromel-alumel thermocouple and found to

give identical readings. The calibration table of emf at low temperature was obtained from the Handbook of Chemistry and Physics.

The intensities from each scan are contained in a set of IBM cards with the conditions under which the experiment are carried out. A Fortran program (Goldak 1964) reduces the measured intensity to a corrected intensity by dividing by the Lorentz-polarization factor and the theoretical atomic scattering factor squared. Values of the theoretical atomic scattering factors by Freeman and Watson (1961) are used. The atomic scattering factors for copper-nickel alloys are obtained by interpolating between the values of copper and nickel.

The program sums 5 readings (1 card in this thesis) to give the total intensity over an angular increment of 0.025° theta. The corrections are performed on 1620 IBM computer. The output from the computer contains the scattering angle, the integrated intensity, and the intensity of an increment. The scattering angle is the position midway between the increment. The integrated intensity, which is the sum of the intensities of the increments, can be obtained for any angular increment. The total intensity (Bragg reflection plus background) is then the sum of the intensities of the increments over the angular range scanned (approximately 11 degrees two theta).

The background is taken as the lowest value of the intensity, averaged from both sides of the peak. Because of small fluctuations in the intensities, an average value is taken over an angular increment of

0.50° theta. This average value together with the average value obtained from the opposite side of the Bragg reflection multiplied by the angular increment between the averaged background values gives the total background. It is assumed that the background is linear between the averaged values. Subtracting the total background from the total intensity in the same angular increment gives the integrated intensity of the Bragg reflection.

The integrated intensities of the Bragg reflections obtained from the corrected intensities can be used to solve equation 4 for the Debye temperature. Goldak (1964) has also written a Fortran program which solves equation 4. The data necessary to solve this program are the integrated intensities and Bragg angles at room temperature and liquid nitrogen temperature, the values of the two temperatures, the wavelength of the radiation (weighted wavelength $2/3\lambda_1 + 1/3\lambda_2$), a constant which contains the factor $\frac{12h^2}{mk}$ (where h is Planck's constant, k is Boltzmann's constant and m is the atomic weight), and an estimated Debye temperature. The Bragg angles used in solving the Fortran program are also weighted with the same proportions as the wavelengths.

RESULTS

(a) Hardness Measurements

Figures 5, 6, and 7 show the effect of composition on micro-hardness. Table 1 contains the data from which the graphs were plotted.

If an imaginary straight line is drawn through the DPH values of pure copper and pure nickel, the maximum deflection from this straight line occurs near 60 atomic percent nickel. The DPH limits shown for each of the points were obtained by replacing the diameter of the indentation squared in equation 8 by the values corresponding to the standard deviation. The standard deviation has been calculated from 50 indentations made for each of the three loads (18, 27, and 35.5 grams). The notation $(+\sigma)$ and $(-\sigma)$ in Table 1 refer to this variation in the diameter of the arithmetic mean diagonal as computed from the standard deviation.

Variation in the diagonals is present even when extreme care has been used in preparing the specimens. In most cases the test indentation is not exactly square but slightly rhombic so that the two diagonals are unequal. This unevenness arises because impressions are made entirely within a single grain; hence the shape and size of the indentation depends on the slip system of the particular grain in which the indentation is placed. However, it is hoped that when 50 indentations are taken at random over the surface of the specimen, and the horizontal and vertical diagonals of each of these indentations are measured separately, a representative value(the mean diagonal of the two measurements) of the size of the impression

Table 1. Data for Plotting Hardness Curves

Alloy	Weight (grams)	Divisions (length scale)	Standard deviation (σ)	Length of diagonal (microns)			Micro-hardness (DPH)		
				($+\sigma$)	(ave.)	($-\sigma$)	($+\sigma$)	(ave.)	($-\sigma$)
Cu	18	150	3	24.6	24.2	23.7	55.0	57.2	59.6
	27	184	7	30.7	29.6	28.5	52.9	57.0	61.7
	35.5	212	4	34.8	34.1	33.5	54.4	56.4	58.7
Cu-20Ni	18	130	3	21.4	20.9	20.4	72.8	76.2	79.9
	27	162	3	26.6	26.1	25.6	70.9	73.6	76.4
	35.5	185	4	30.4	29.8	29.1	71.1	74.2	77.5
Cu-40Ni	18	122	3	20.1	19.6	19.1	82.4	86.5	90.9
	27	149	3	24.5	23.9	23.5	83.6	87.0	90.6
	35.5	171	3	28.0	27.5	27.0	83.9	86.8	89.9
Cu-60Ni	18	115	3	18.9	18.5	18.0	92.5	97.3	102.7
	27	141	3	23.2	22.7	22.2	93.2	97.2	101.4
	35.5	163	3	26.7	26.2	25.8	92.2	95.6	99.2
Cu-80Ni	18	118	2	19.3	18.9	18.7	89.4	92.5	95.7
	27	143	3	23.2	22.7	22.2	90.6	94.5	98.5
	35.5	164	3	26.9	26.4	25.9	91.1	94.4	97.9
Ni	18	132	3	21.7	21.2	20.8	70.7	73.9	77.4
	27	162	2	26.4	26.1	25.8	71.8	73.6	75.5
	35.5	187	3	30.6	30.1	29.6	70.4	72.6	75.0

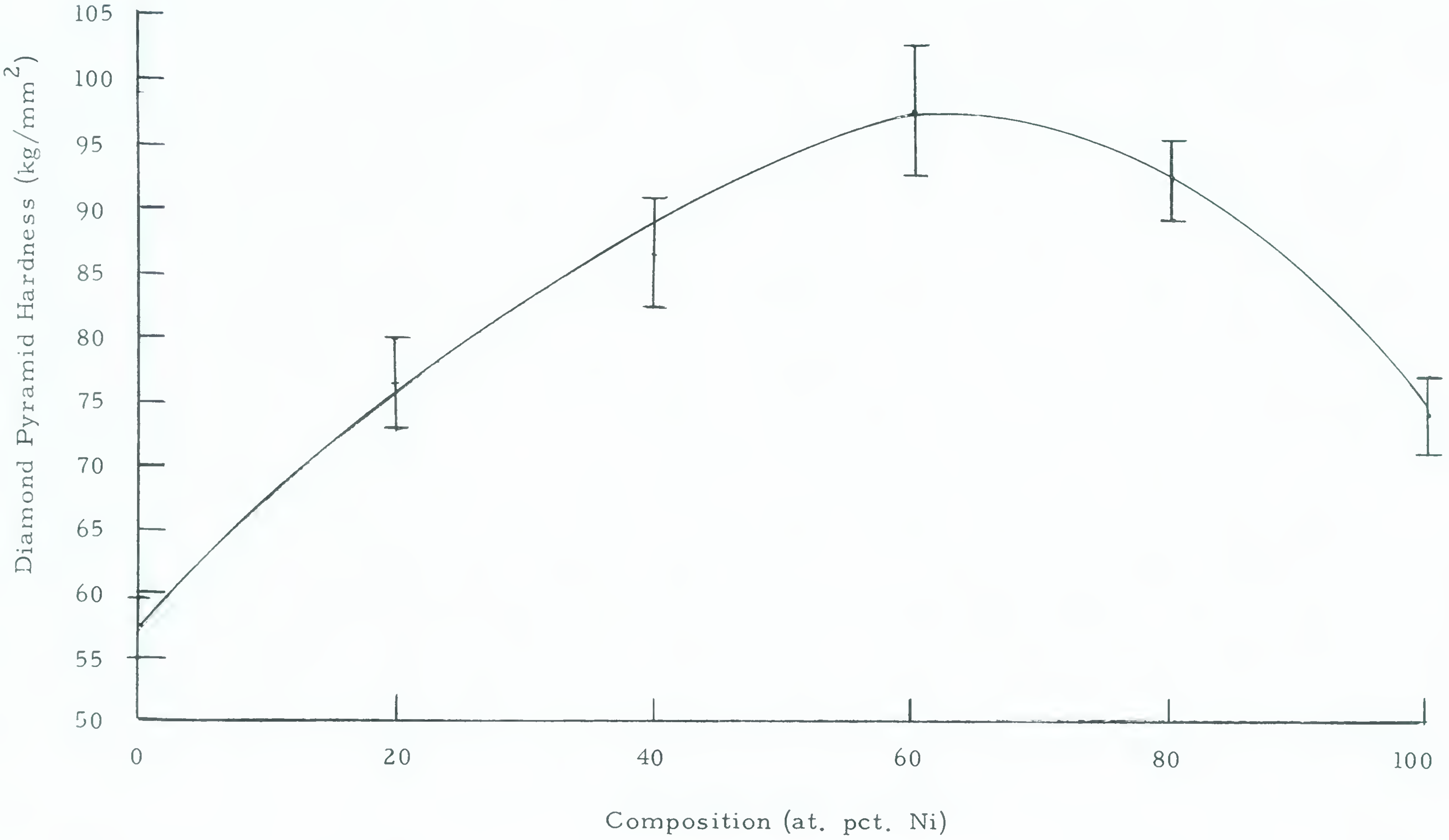

Figure 5. Hardness Curve (18 gram load)

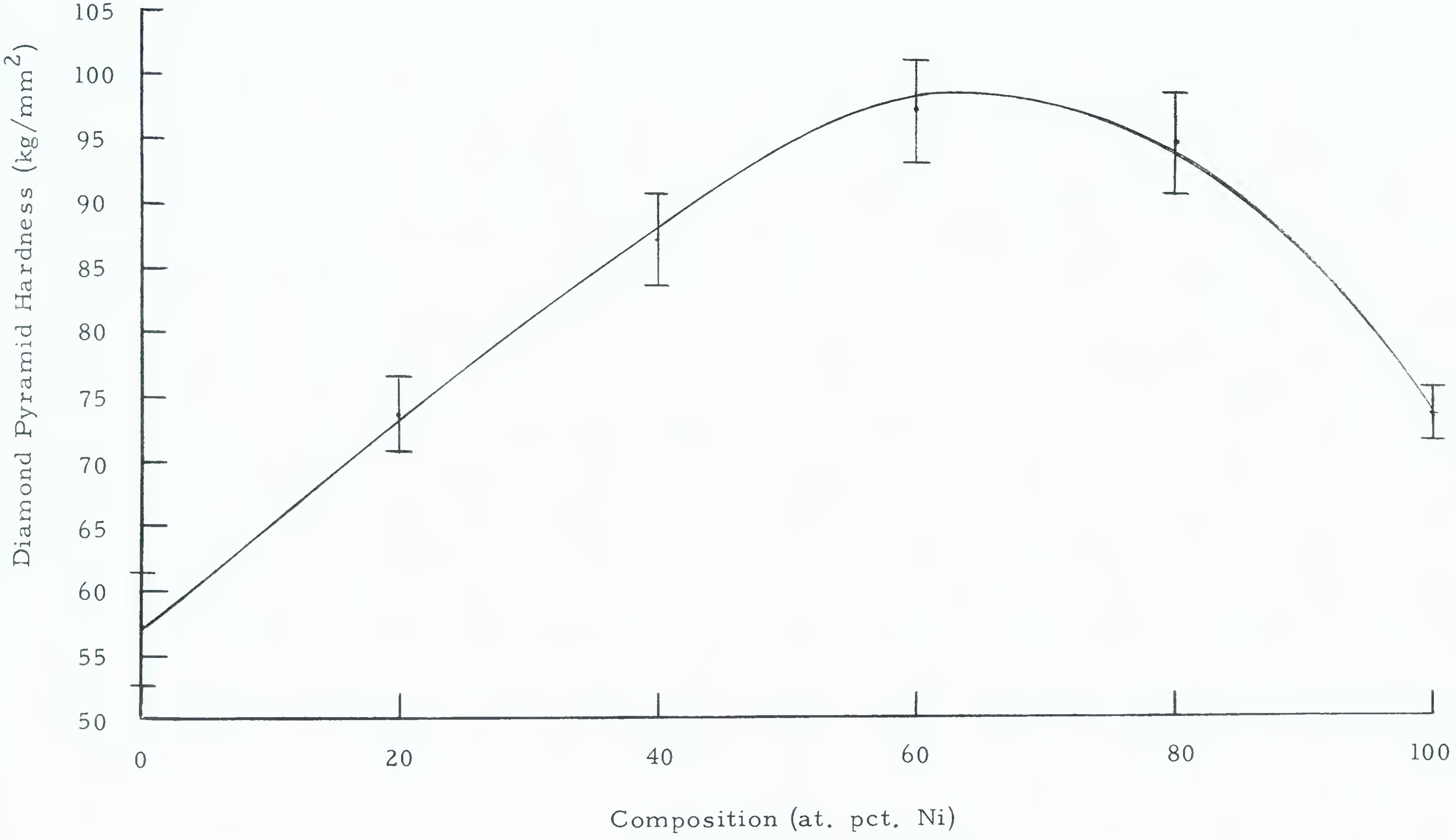

Figure 6. Hardness Curve (27 gram load)

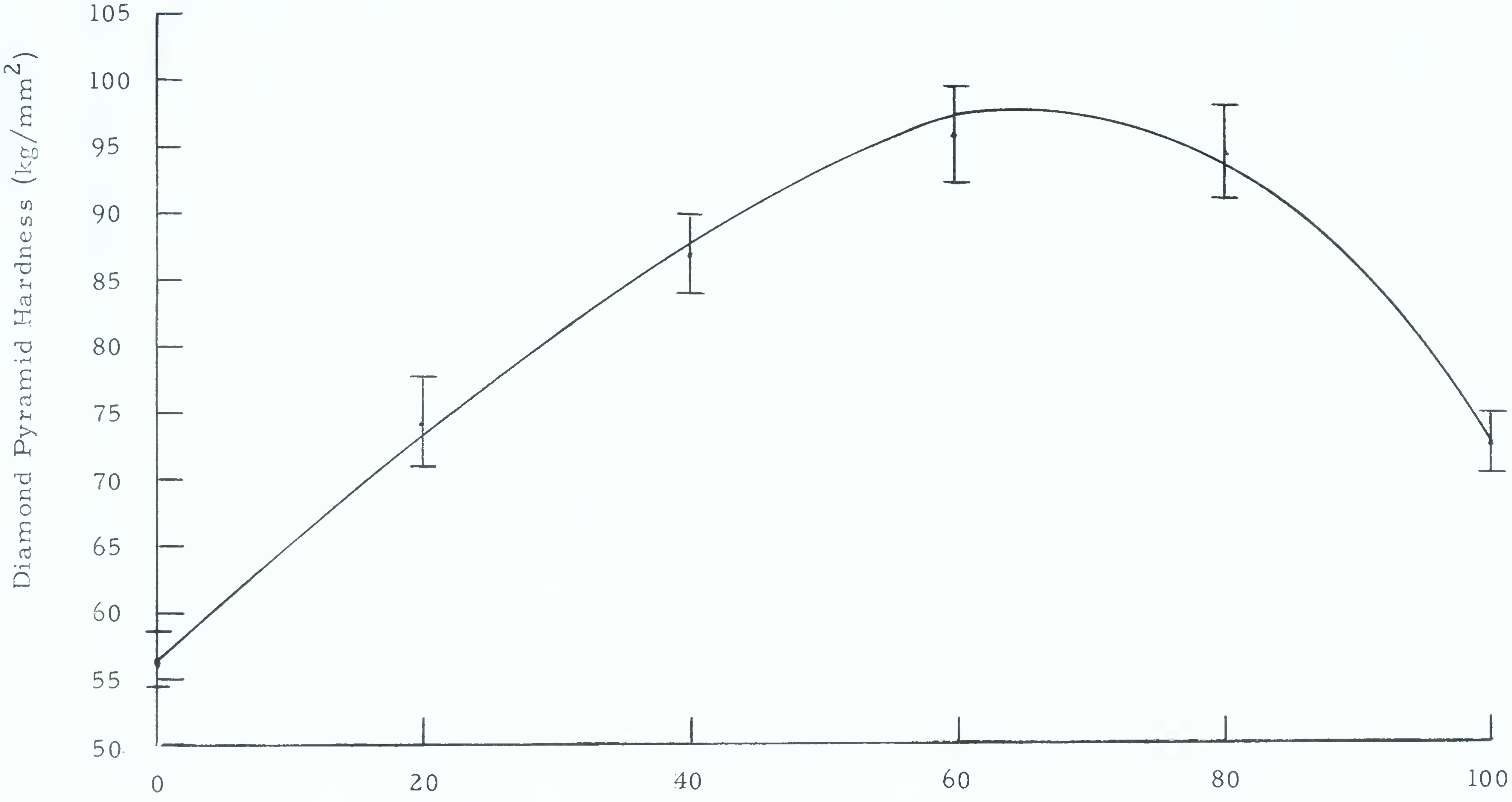

Figure 7. Hardness Curve (35.5 gram load)

can be expected. It is the arithmetic mean which is shown in column 4, Table 1 and is the middle point of the three points plotted in Figures 5, 6, and 7.

The most common standard deviation was 3, although copper shows deviations of 7 and 4 for loads of 27 and 35.5 grams respectively. Since copper is the softest of the materials tested the work hardened layer has perhaps not been sufficiently removed. If a slightly different procedure in preparing the copper specimen for micro-hardness measurements were to be used (annealing the specimen before the final etch) it is conceivable that the standard deviation could be lowered.

The DPH values shown in the last three columns of Table 1 do not show a marked dependence on the applied load. However, where a dependence exists, a relationship between the load applied (P) and diameter of indentation (d) can be expressed in the following manner,

$$P = ad^{n} \qquad (9)$$

where a and n are constants for a given material. The constant n is referred to as the Meyer exponent and is assumed to be constant within the range of values found in this work.

By combining equations 8 and 9 the following relationship is obtained for DPH,

$$\mathrm{DPH} = 1854.4ad^{n-2} \quad \mathrm{kg/mm^2} \qquad (10)$$

where a has the same notation as above and n is the Meyer exponent. The exponent n varies about 2. When n is equal to 2, a constant hardness value is implied, whatever the value of the applied load or the impression size, whereas with n not equal to 2, the micro-hardness depends upon the load applied.

The value of the Meyer exponent, n, can be found by plotting the logarithm of the load applied (P) against the logarithm of the indentation diagonal (d), as in Figure 8. Because of experimental errors, the points corresponding to the various weights employed do not lie on a straight line but are slightly scattered. Therefore, to avoid any arbitrariness (which is unavoidable in graphical interpolations) the method of least squares is used to obtain the Meyer exponent. By taking logarithms of equation 9, a linear equation relating log P and log d is obtained,

$$\log P = n \log d + \log a \qquad (11)$$

According to the method of least squares the constant n, the Meyer exponent, is obtained as follows,

$$n = \frac{k\Sigma \log d \log P - \Sigma \log d \log P}{k\Sigma(\log d)^2 - (\Sigma \log d)^2} \qquad (12)$$

Table 2 contains the data used to solve for the Meyer exponent for the range of alloys; k is the number of values used in obtaining the straight line (3 in this case). Table 3 contains the values of the Meyer exponent and the 80 percent confidence limits. However, due to the restricted

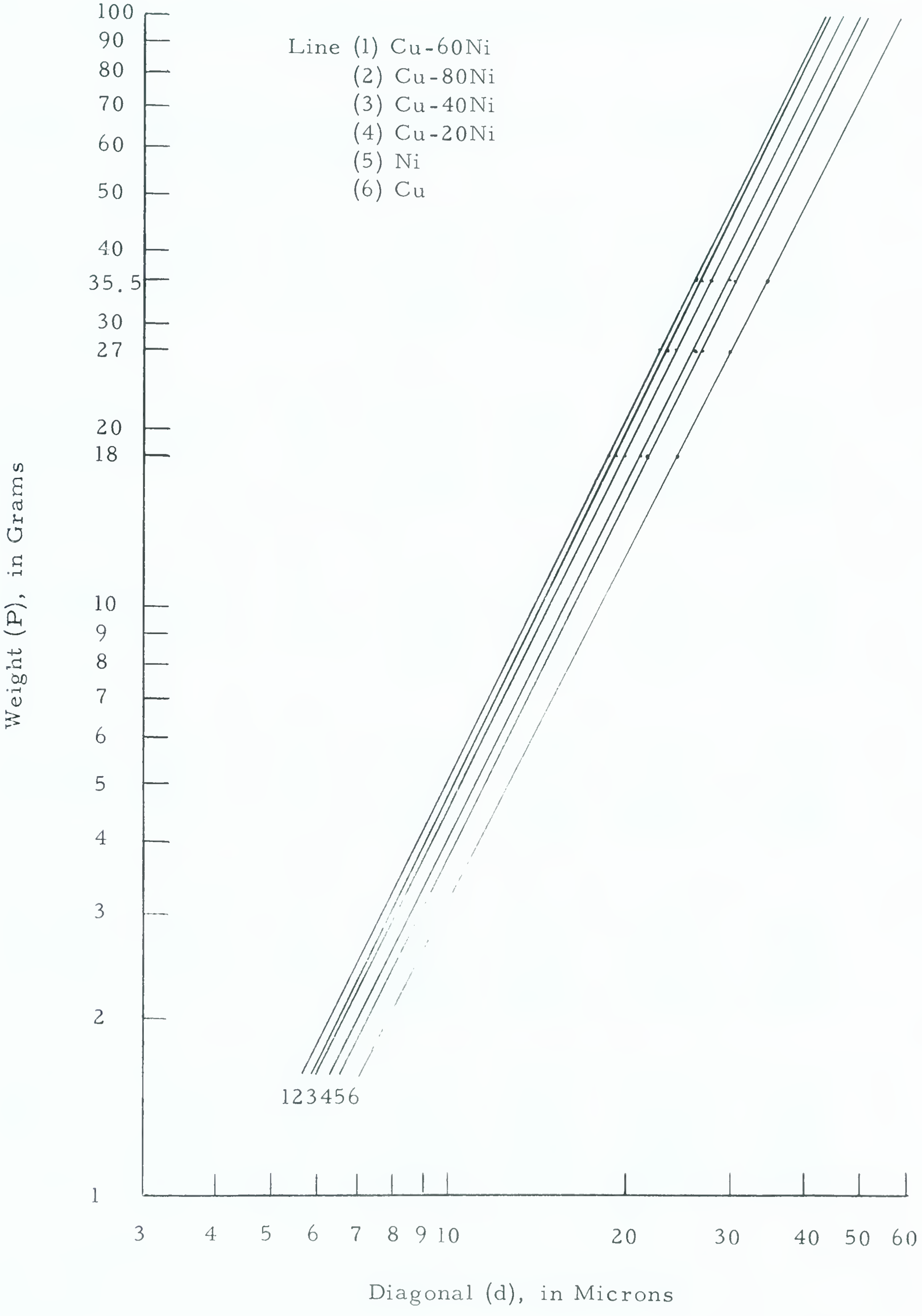

Figure 8. The 'Meyer Lines'

Table 2. Data for Obtaining Meyer Exponent

Alloy	Diagonal (microns)	Weight (grams)	log d	log P	$(\log d)^2$	log d log P
Cu	24.2	18	1.3838	1.2553	1.9149	1.7371
	29.6	27	1.4713	1.4313	2.1647	2.1060
	34.1	35.5	1.5328	1.5502	2.3495	2.3761
			4.3879	4.2369	6.4291	6.2192
Cu-20Ni	20.9	18	1.3201	1.2552	1.7427	1.6571
	26.1	27	1.4166	1.4314	2.0068	2.0277
	29.8	35.5	1.4742	1.5502	2.1733	2.2853
			4.2109	4.2369	5.9228	5.9701
Cu-40Ni	19.6	18	1.2923	1.2553	1.6700	1.6222
	23.9	27	1.3784	1.4314	1.8999	1.9730
	27.5	35.5	1.4393	1.5502	2.0716	2.2312
			4.1100	4.2369	5.6415	5.8264
Cu-60Ni	18.5	18	1.2672	1.2553	1.6058	1.5907
	22.7	27	1.3560	1.4314	1.8387	1.9409
	26.2	35.5	1.4183	1.5502	2.0116	2.1986
			4.0415	4.2369	5.4561	5.7302
Cu-80Ni	18.9	18	1.2765	1.2553	1.6295	1.6024
	22.7	27	1.3560	1.4314	1.8387	1.9409
	26.4	35.5	1.4216	1.5502	2.0209	2.2038
			4.0541	4.2369	5.4891	5.7471
Ni	21.2	18	1.3263	1.2553	1.7591	1.6649
	26.1	27	1.4166	1.4314	2.0068	2.0277
	30.1	35.5	1.4786	1.5502	2.1863	2.2921
			4.2215	4.2369	5.9522	5.9847

Table 3. Values of Meyer Exponent and 80% Confidence Limits

Alloy	Meyer Exponent	80% Confidence Limits
Cu	1.98	± 0.18
Cu-20Ni	1.88	± 0.36
Cu-40Ni	2.07	± 0.58
Cu-60Ni	1.94	± 0.33
Cu-80Ni	2.04	± 0.26
Ni	1.92	± 0.35

range of loads used in determining the Meyer exponent and the limited range of DPH values, it is impossible to come to any conclusions about the Meyer exponents. Further, it cannot be concluded that the Meyer exponent will continue in the manner shown in the straight line relationship of Figure 8. It is quite probable that if a log P/log d curve is drawn for the complete range of loads (micro plus macro range) the Meyer exponent will lie between two asymptotes of slope n equal to 2. This is equivalent to saying that hardness tends to assume constant values not only for increasing loads (classic macro-hardness), but also for decreasing loads, a fact which is certainly not evident here.

It may then be concluded that the DPH values can only be used for comparison purposes and not as absolute values.

(b) Errors Affecting the Hardness Values

The chief sources of error that arise in micro-hardness testing has been reported by Buckle (1959). He mentions a number of individual causes and gives examples of their effect on the measurement.

When making micro-hardness measurements a similar procedure is followed before making indentations and during the actual making of the impressions. The weight scale is checked before making a set of indentations, to see if any variation from the calibration curve plotted in Figure 4 (see section on Reichert Micro-hardness Tester) occurred. The time of holding the diamond in the test material is constant (10 seconds) and the time of loading, i.e. applying the load to the maximum value, is similar

for each load and specimen. It is hoped that this consistency will minimize systematic errors.

Buckle (1959) claimed if measurements are taken on one instrument by the same person that a variation of indentation diameter of the order of 0.5 microns is possible. This value corresponds very favorably with the standard deviation obtained from most of the materials tested here.

A standard deviation of one corresponds to one division on the divided drum of the measuring eyepiece, which is equal to 0.161 microns in the field of observation. Taking the common standard deviation of 3, and converting to microns, it becomes 0.483 or 0.5 when rounded off. If instrumental errors are considered together with the nature of the specimen and its surface, it is probable that the hardness values could scatter more. This is very readily observed from the results in the previous section. However, the fact that the value of the standard deviation corresponds with Buckle's value shows that the DPH results have fallen within the expected human error.

(c) Integrated Intensities and Debye Temperatures

The integrated intensity measurements for room and liquid nitrogen temperatures are shown in Table 4. The average integrated intensities and the percent standard deviation are shown at the bottom of each column for each specimen. It is these average integrated intensities which are used to obtain the Debye temperatures. Also shown in Table 4 are the two theta angle and the temperature at which the reflected intensities

were measured. The two theta angle corresponds to a weighted angle ($2/3\ \phi_1 + 1/3\ \phi_2$). Values for nickel are not shown in Table 4 as Goldak (1964) has made extensive studies on nickel and his result for the Debye temperature is used in this work. The method by which he obtained the Debye temperature is identical to the procedure used in this work except that his measurements have been made on 28 runs.

A plot of Debye temperature versus atomic percent nickel is shown in Figure 9, but because of the small number of intensity measurements (5 scans) the limits should be treated cautiously. A maximum deflection occurs near 60 atomic percent nickel.

(d) Errors Affecting the Computed Debye Temperature

Integrated intensity measurements were obtained on an apparatus designed and built by Goldak (1964). Since only the relative change in the integrated intensity was sought, alignment errors in the apparatus will not affect the results provided they remain constant for all the scans. If absolute measurements were recorded the matter of alignment would be critical. However, only the change observed in a particular specimen is relevent to this work. To insure that alignment errors would not affect the results in any one sample, all scans were made in the forward direction. Goldak (1964) has reported the optical alignment to be accurate to 1 minute of arc. It is therefore believed that the system contributes no significant error to the intensity measurements.

The most serious errors arise in attaching a value to the background

Table 4. Summary of Integrated Intensity Measurements

Alloy	Integrated Intensity	2θ	Temp (mv)	Integrated Intensity	2θ	Temp (mv)
Cu	166.4	103.7	1.07	382.2	104.0	-5.62
	164.2	103.7	1.05	376.7	104.0	-5.62
	165.9	103.7	1.04	387.5	104.0	-5.62
	166.1	103.7	1.05	387.7	104.0	-5.62
	164.9	103.7	1.06	383.5	104.0	-5.62
ave.	165.5	103.7	1.05	383.5	104.0	-5.62
std. dev.	0.5 %			1.1 %		
Cu-20Ni	228.3	104.6	1.07	395.4	105.0	-5.62
	207.4	104.6	1.05	380.4	105.0	-5.62
	213.7	104.6	1.05	396.6	105.0	-5.62
	209.1	104.6	1.06	399.5	105.0	-5.62
	216.2	104.6	1.04	400.7	105.0	-5.62
ave.	214.9	104.6	1.05	394.5	105.0	-5.62
std. dev.	3.4%			1.8%		
Cu-40Ni	265.4	105.3	1.06	402.4	105.7	-5.62
	265.5	105.3	1.06	381.5	105.7	-5.62
	265.3	105.3	1.07	393.9	105.7	-5.62
	264.4	105.3	1.10	398.3	105.7	-5.62
	263.2	105.3	1.11	391.4	105.7	-5.62
ave.	264.8	105.3	1.08	393.5	105.7	-5.62
std. dev.	0.3%			1.8%		
Cu-60Ni	379.5	106.0	1.04	808.8	106.4	-5.62
	359.1	106.0	1.02	801.7	106.4	-5.62
	375.6	106.0	1.02	790.3	106.4	-5.62
	338.5	106.0	1.03	807.5	106.4	-5.62
	347.6	106.0	1.03	791.4	106.4	-5.62
ave.	360.1	106.0	1.03	799.9	106.4	-5.62
std. dev.	4.4%			1.0%		
Cu-80Ni	302.9	106.8	1.08	565.0	107.2	-5.62
	300.6	106.8	1.08	560.9	107.2	-5.62
	289.8	106.8	1.09	560.9	107.2	-5.62
	299.7	106.8	1.08	562.4	107.2	-5.62
	284.3	106.8	1.08	568.7	107.2	-5.62
ave.	295.5	106.8	1.08	563.7	107.2	-5.62
std. dev.	2.4%			0.5%		

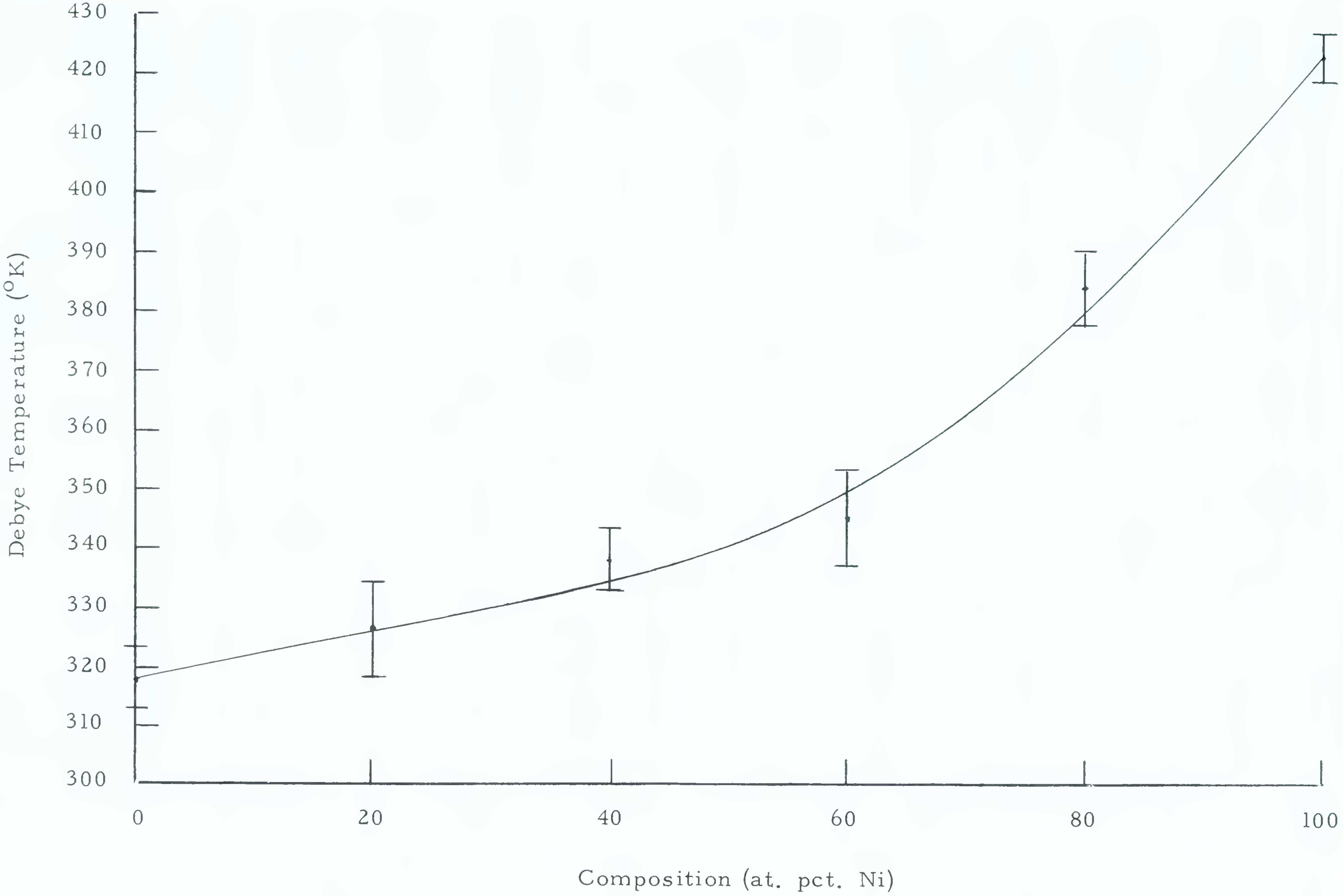

Figure 9. Debye Temperature Values

intensity, and (to a much smaller extent) in the reliability of the temperature reading.

Temperatures are measured with a 4725 Rubicon Potentiometer which can be read to one microvolt. The reference temperature used in conjunction with the potentiometer is an ice bath at 0°C. The temperature reading of each specimen was observed to be higher than the boiling point of liquid nitrogen by 5 degrees K. This is attributed to the mechanical connection between the specimen and the cryostat. A thermocouple placed at a point approximately where the x-ray beam hits the specimen showed the temperature to be identical to that measured by a thermocouple in the backing block. The temperature reading is considered to be accurate to 1°K.

The x-ray photons generated by the anode of the x-ray tube are emitted in a random manner with respect to time. Hence, the quanta arriving at the scintillation counter are also random in time, and the intensity measurements will therefore be governed by the laws of probability. Since the counter can record only one reflection at a time, time limitations generally prohibit the counting of sufficient photons to reduce the statistical errors to a vanishing point. The magnitude of the statisical error depends only upon the total number of quanta (photons) counted. Then the relative standard deviation U, in the intensity, is calculated from

$$U = \frac{1}{N^{\frac{1}{2}}} \tag{13}$$

where N is the number of counts observed. The relative probable error is 0.675 U. It follows then, that the probable error in the background intensity will be larger than that in the Bragg peak. Because of the large peak-to-background ratios observed here, the relative error in the Bragg reflection caused by error in estimating the background intensity is small. Further, at higher scattering angles the background is more uniform, which permits a considerable improvement in isolating the Bragg reflection.

The limits for the Debye temperature shown in Figure 9 have been obtained by adding the percent standard deviation for each set of average intensities (room temperature and liquid nitrogen temperature) and inserting these values in the Fortran program.

DISCUSSION

There are two aspects to the discussion of experimental results:

(a) a comparison of Debye temperatures measured by the diffracted intensity method and those computed from the Debye formula (which depends upon factors that include elastic modulus),

(b) a possible relationship between Debye temperatures and hardness of copper-nickel alloys.

(a) Comparison of Debye Temperatures.

There are a number of methods of determining the Debye temperature of a solid. These depend differently on the deviation of the true frequency spectrum from its assumed parabolic form. Two of the methods will be mentioned here, one of which has already being explained; the other method is explained below. It is important to determine whether the values of the Debye temperature obtained from various experiments can be used interchangeably.

Debye temperatures may be computed from the elastic constants by an equation derived by Debye and given in James (1948):

$$\Theta = \frac{h3^{\frac{1}{2}}}{k}\left(\frac{3N}{4\pi}\right)^{\frac{1}{3}}\frac{E^{\frac{1}{2}}\,f(v)}{m^{\frac{1}{3}}\,d^{\frac{1}{6}}} \qquad (14)$$

where Θ = Debye temperature

h = Planck's constant

k = Boltzmann's constant

N = Avogadro's number

$E =$ Young's modulus

$m =$ atomic weight

$d =$ density

$f(v) =$ a function depending on Poisson's ratio

Because $f(v)$ is insensitive for values of Poisson's ratio in the range $0.2 < v < 0.5$ (copper $= 0.34$, nickel $= 0.31$) a simpler approximation can be given which is valid for face-centered cubic materials:

$$\Theta \approx 12 \left(\frac{E\,a}{A}\right)^{\frac{1}{2}} \tag{15}$$

where $E =$ Young's modulus in kg/mm^2

$A =$ atomic weight

$a =$ lattice parameter in angstroms

If values of Young's modulus, lattice parameter and atomic weight for copper and nickel are substituted in equation 15, the Debye temperatures correspond very favorably with the values computed from the integrated intensity measurements (Table 5). The problem of calculating Debye temperatures for copper-nickel alloys is more difficult, for if one assumes Young's modulus to vary linearly with composition, a straight line relation is obtained. This straight line follows very close to the imaginary straight line drawn between the Debye temperature values of pure copper and pure nickel obtained by intensity measurements. A comparison is shown in Table 5. The lattice parameters are known to obey Vegard's law (Pearson 1958), and the atomic weight of copper is

Table 5. Values of Debye Temperatures

Alloy	Young's modulus (kg/mm^2)	Debye Temperatures elastic properties	imaginary straight line	integrated intensities
Cu	112×10^2	310	317	317
Cu-20Ni	130×10^2	330	339	326
Cu-40Ni	151×10^2	354	360	338
Cu-60Ni	172×10^2	380	382	345
Cu-80Ni	189×10^2	400	402	384
Ni	210×10^2	425	423	423

similar to nickel: therefore, one is forced to conclude either that Young's modulus does not obey the law of mixing, or the formula for obtaining the Debye temperatures from elastic constants is far too simple for use here. The basic assumptions of the Debye approximation, which assumes simple harmonic vibrations, an isotropic solid with no dispersion, are not realized in practice and hence lead to restrictions on the applicability of the theory. Reliable vibrational spectra have been determined for a number of metals and these are very different from the corresponding parabolic forms. As has already been mentioned, the Debye approximation is restricted to crystals containing only one type of atom in a simple lattice. It is quite probable then, that the simple elastic vibrations assumed present for the copper-nickel alloys is not adequate and prevents a satisfactory comparison of the two methods. Therefore, without obtaining the Debye temperature by another independent method (by specific heat measurements, say) for comparison a definite conclusion cannot be reached about which of the two methods gives the more reasonable results.

(b) Relationship Between Hardness and Debye Temperature.

It can be seen from Figures 5, 6, 7, and 9 that the graphs of Debye temperature versus composition, and micro-hardness versus composition, all show a maximum deflection from linearity near 60 atomic percent nickel. The question now arises whether there is a relationship between Debye temperature and micro-hardness values.

It has been shown that when a hard indenter is forced into the surface of another material under controlled conditions, the size of the indentation remaining is directly related to the composition. Now, the hardness of materials does not involve a single physical property, but usually involves both the elastic and plastic deformation characteristics of the material. The deformation is predominantly outside the elastic range and involves considerable plastic deformation. For this reason, the hardness of metals is bound up primarilywith their plastic properties and only to a secondary extent with their elastic properties.

Because the indentations are made in large grains (in effect, single crystals) it was believed that a relationship could be found between Peierls force and hardness. Peierls force is defined as the force (F) opposing the glide motion of a dislocation in the crystal lattice, and may be represented by

$$F = \frac{2Gb^2}{(1-v)a} \sin 4\pi x \ \exp\left(\frac{-4\pi w}{b}\right)$$

where G = shear modulus

b = atomic spacing in the shear direction

a = atomic spacing between rows of atoms

v = Poisson's ratio

w = 'width' of the dislocation

x = a variable depending on the displacement of the dislocation from the nearest position of symmetry

The relation between the shear modulus, G, and Young's modulus, E, is

$$G = \frac{E}{2(1+v)}$$

Hence, Peierls force can be related to the elastic properties of the material.

In all crystals, imperfections, including dislocations, exist to an extent depending largely on the history of the crystal. When the material is plastically deformed, as it is when impressions are made in the surface, these dislocations move through the crystal lattice. Peierls, in calculating the force opposing this movement assumes a single dislocation placed symmetrically in an otherwise unstrained lattice. If the dislocation in the unstrained lattice is displaced a little, this displacement is opposed by a force (Peierls force). The force is set up when atoms in the slip plane on opposite sides of the dislocation no longer lie in equivalent positions in the periodic field of the plane. By examining how the energy of misfit between the faces of the slip plane changes as the dislocation moves from one position of symmetry to the next, Peierls was able to calculate the above formula. The maximum force required to move a dislocation occurs when $4\pi x = 1$.

It was hoped that if the Peierls force could in some way be represented by the hardness values, Young's modulus could be obtained and the problem of showing a connection between hardness and Debye temperature would be solved. For having obtained Young's modulus, the value could be used

in the Debye formula to obtain the Debye temperature.

The approximations used in finding the Peierls force are highly idealized. The main uncertainity arising is the calculation of the width of the dislocation, where its magnitude can only be estimated. The width of the dislocation depends on the nature of the interatomic forces, the actual dependence of the restoring force on the atomic displacement and on the temperature. Because of this sensitivity 'the Peierls force cannot be predicted within a factor of 10^4' (van Bueren 1961).

There are also numerous other factors which prohibit the use of the Peierls force as the connection between hardness and Debye temperatures. The plastic deformation that occurs during the making of an impression is more complex than that which is used in deriving the Peierls force, and the glide motion of dislocations is usually far more hindered by the presence of other lattice imperfections, which Peierls assumes are not present. The pinning of dislocations by point defects, the interaction of dislocations, the presence of impurities, along with many other factors which contribute to opposing the movement of dislocations are all neglected by Peierls in his treatment. These effects would be particularly important in the micro-hardness region where the influence of structural and experimental factors predominate. It is reasonable to conclude therefore, that the Peierls force (as it is represented by Peierls formula) plays an insignificant role in the plastic behavior of metals during the indentation process of hardness measurements.

Attempts have been made by many other investigators (Tabor 1951, Buckle 1959, Mott 1956) to show a relationship between hardness and the ultimate tensile strength of the material. However, all this work has been done in the macro-hardness region; and the relationship between ultimate tensile strength and elastic moduli is not well known. The main problem in showing a relation between Debye temperatures and hardness values has been to obtain a connection from the standpoint of the elastic properties of the material. But as mentioned at the beginning of this discussion, the indentations produced in the surfaces of crystals involve predominantly the plastic properties and to a lesser extent the elastic properties. These two properties, when they are related to a hardness measurement; cannot be separated, and even when the plastic component is separately considered, the role played by the elastic modulus cannot be analyzed in any but the simplest, idealized case—— which is not pertinent to the hardness measurement. Hence there appears to be no immediately accessable way of correlating the Debye temperatures and the micro-hardness values.

SUMMARY and CONCLUSIONS

(1) The Debye temperature of copper-nickel alloys has been found by measuring the integrated intensity of the 800 reflection at room temperature and liquid nitrogen temperature. The graph shows a maximum deflection from linearity near 60 atomic percent nickel.

(2) Micro-hardness values (DPH) for the copper-nickel system have been obtained for three applied loads, (18, 27, and 35.5 grams) and the Meyer exponent calculated for the range between these loads. The DPH values have a maximum value near 60 atomic percent nickel.

(3) There appears to be no simple correlation between the Debye temperature and hardness values of copper-nickel alloys.

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APPENDIX I

ANALYSES OF:

(a) materials used.

(b) alloys prepared.

(a) materials used

NICKEL SOURCE

From: JOHNSON, MATTHEY & CO., LIMITED

ANALYSIS:

ELEMENT		ESTIMATE OF QUANTITY PRESENT parts per million
Iron		5
Silicon		3
Aluminum		2
Calcium		1
Magnesium		1
Copper) Silver)	each element less than	1

The following elements were sought but not detected:

As, Au, B, Ba, Be, Bi, Cd, Co, Cr, Cs, Ga, Ge, Hf, Hg, In, Ir, K, Li, Mn, Mo, Na, Nb, Os, P, Pb, Pd, Pt, Rb, Re, Rh, Ru, Sb, Se, Sn, Sr, Ta, Te, Ti, Tl, V, W, Zn, Zr.

COPPER SOURCE

From: JOHNSON, MATTHEY & CO., LIMITED

ANALYSIS:	ELEMENT		ESTIMATE OF QUANTITY PRESENT parts per milion
	Iron		2
	Silicon		1
	Silver		1
	Magnesium	less than	1

The following elements were sought but not detected:

Al, As, Au, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cs, Ga, Ge, Hf, Hg, In, Ir, K, Li, Mn, Mo, Na, Nb, Ni, O, P, Pb, Pd, Pt, Rb, Re, Rh, Sb, Se, Sn, Sr, Ta, Te, Ti, Tl, V, W, Zn, Zr.

(b) alloys used

Samples are those cut from ingots which have been induction melted, cold-rolled, and annealed for 12 hours at 1000°C.

Wet Chemical Analysis (U of A laboratory, Department of Mining and Metallurgy).

	Wt. pct. Ni	At. pct. Ni
20-80 Cupro-Nickel*	77.55	78.90
40-60 Cupro-Nickel	57.45	59.38
60-40 Cupro-Nickel	38.40	40.29
80-20 Cupro-Nickel	18.65	19.88

Spectrographic Analysis (CHICAGO SPECRO SERVICE LAB. INC.).

	Wt. pct. Ni	At. pct. Ni
20-80 Cupro-Nickel	77.87	79.71
40-60 Cupro-Nickel	57.40	59.39
60-40 Cupro-Nickel	37.60	39.60
80-20 Cupro-Nickel	18.16	19.35

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* 20-80 Cupro-Nickel denotes an alloy containing approximately 20 atomic percent copper and 80 atomic percent nickel. Both the chemical and spectrographic analysis have been made from portions cut from the same ingot. Only wt. pct. nickel was determined by the wet chemical analysis.

Spectrographic Analysis (CHICAGO SPECTRO SERVICE LAB. INC.).

	Wt. pct. Cu	At. pct. Cu
20-80 Cupro-Nickel	21.46	20.28
40-60 Cupro-Nickel	42.50	40.61
60-40 Cupro-Nickel	62.08	60.40
80-20 Cupro-Nickel	81.79	80.69

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